Catalyst Site Epimerization during the Kinetic Resolution of Chiral α-Olefins by Polymerization.

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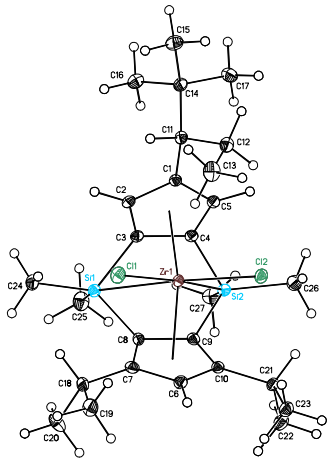
Crystal Structure Data for (*S*)-2

Contents



(*S*)-2

Note: Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 635262.

Table S.1. Crystal data and structure refinement for **(*S*)-2** (CCDC 635262).

Empirical formula	$C_{27}H_{44}Si_2Cl_2Zr$
Formula weight	586.92
Crystallization Solvent	Not given
Crystal Habit	Plate
Crystal size	0.25 x 0.22 x 0.07 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKa
Data Collection Temperature	100(2) K
θ range for 24444 reflections used in lattice determination	2.27 to 40.09°
Unit cell dimensions	a = 8.7249(3) Å b = 11.4772(4) Å c = 28.8269(11) Å
Volume	2886.65(18) $Å^3$
Z	4
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.351 Mg/m^3
F(000)	1232
Data collection program	Bruker SMART v5.630
θ range for data collection	1.91 to 40.60°
Completeness to θ = 40.60°	92.3 %
Index ranges	$-15 \le h \le 15$, $-19 \le k \le 18$, $-52 \le l \le 50$
Data collection scan type	ω scans at 7 ϕ settings
Data reduction program	Bruker SAINT v6.45A
Reflections collected	67983
Independent reflections	16445 [R_{int}= 0.0944]
Absorption coefficient	0.663 mm^{-1}
Absorption correction	None

Max. and min. transmission	0.9551 and 0.8518

Table S.1 (cont.)

Structure solution and Refinement

Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	16445 / 0 / 301
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.091
Final R indices [I>2σ(I), 12573 reflections]	R1 = 0.0393, *w*R2 = 0.0663
R indices (all data)	R1 = 0.0609, *w*R2 = 0.0698
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Absolute structure determination	Anomalous differences
Absolute structure parameter	-0.031(19)
Largest diff. peak and hole	0.778 and -0.557 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

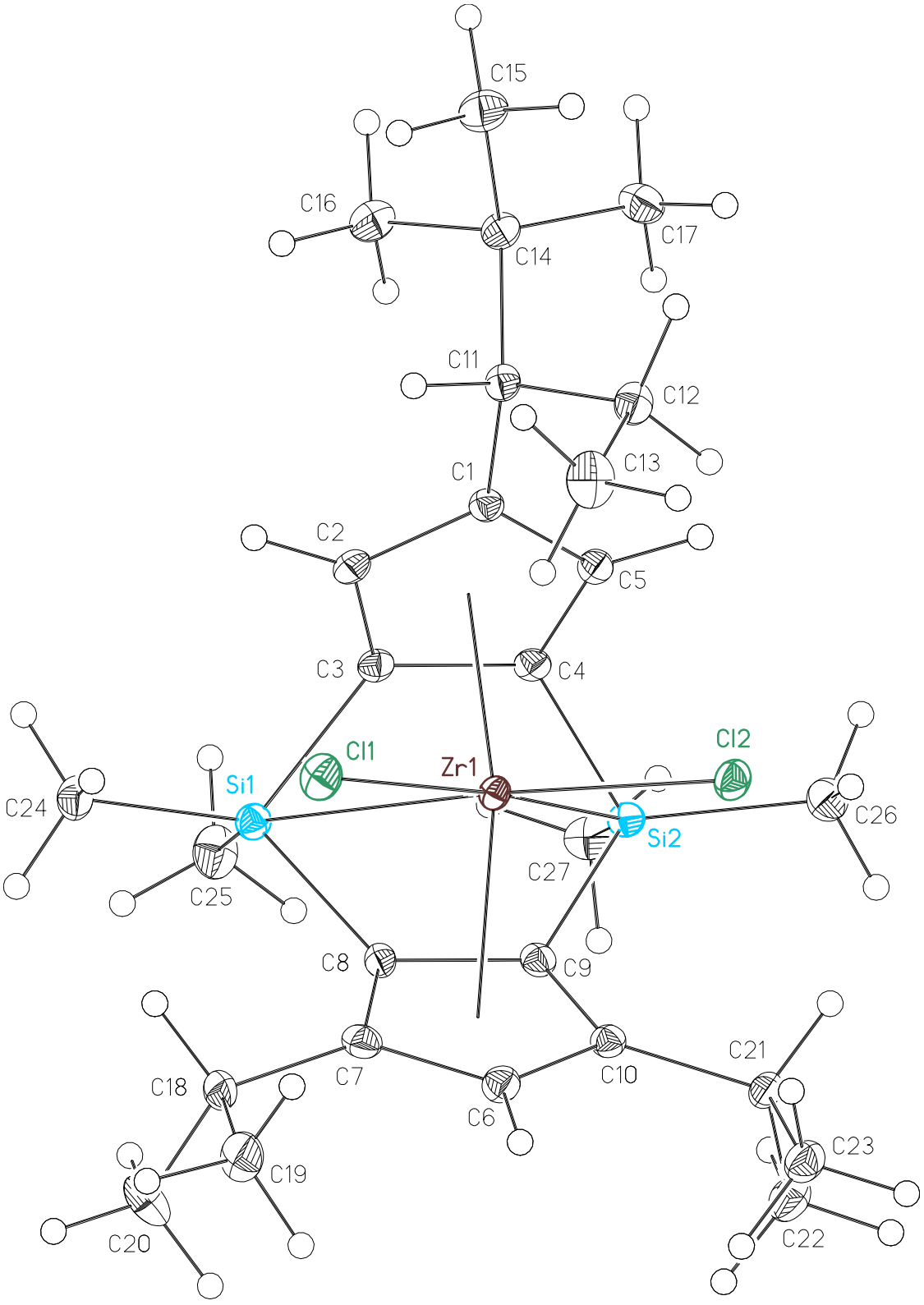


Figure S.1 Minimum overlap view of **(*S*)-2**.

Table S.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **(*S*)-2** (CCDC 635262). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Zr(1)	387(1)	8003(1)	1238(1)	9(1)
Cl(1)	-347(1)	7967(1)	422(1)	16(1)
Cl(2)	-813(1)	9758(1)	1543(1)	14(1)
Si(1)	2322(1)	5631(1)	1204(1)	11(1)
Si(2)	1918(1)	7286(1)	2211(1)	10(1)
C(1)	2954(2)	9150(2)	1035(1)	10(1)
C(2)	3066(2)	7988(2)	869(1)	11(1)
C(3)	2971(2)	7187(1)	1249(1)	11(1)
C(4)	2781(2)	7892(2)	1666(1)	10(1)
C(5)	2773(2)	9076(2)	1521(1)	11(1)
C(6)	-2068(2)	6747(2)	1482(1)	13(1)
C(7)	-1070(2)	6022(1)	1224(1)	13(1)
C(8)	375(2)	5975(1)	1455(1)	10(1)
C(9)	218(2)	6664(1)	1887(1)	11(1)
C(10)	-1321(2)	7096(2)	1896(1)	11(1)
C(11)	3201(2)	10237(2)	744(1)	11(1)
C(12)	2066(2)	11228(2)	859(1)	14(1)
C(13)	653(2)	11209(2)	544(1)	21(1)
C(14)	4928(2)	10620(2)	761(1)	13(1)
C(15)	5200(2)	11540(2)	384(1)	19(1)
C(16)	5981(2)	9584(2)	665(1)	17(1)
C(17)	5359(2)	11140(1)	1234(1)	17(1)
C(18)	-1567(2)	5334(2)	800(1)	15(1)
C(19)	-3108(2)	5731(2)	611(1)	20(1)
C(20)	-1635(2)	4041(2)	932(1)	24(1)
C(21)	-2112(2)	7701(2)	2297(1)	12(1)
C(22)	-2239(2)	6826(2)	2700(1)	17(1)
C(23)	-3704(2)	8145(2)	2161(1)	16(1)
C(24)	2337(2)	5186(2)	584(1)	16(1)
C(25)	3425(2)	4513(2)	1538(1)	20(1)
C(26)	1462(2)	8509(2)	2615(1)	17(1)
C(27)	3119(2)	6224(2)	2536(1)	16(1)

Table S.3. Selected bond lengths [Å] and angles [°] for **(*S*)-2** (CCDC 635262).

Zr(1)-Cl(2)	2.4356(4)	Cl(2)-Zr(1)-Cl(1)	104.467(15)
Zr(1)-Cl(1)	2.4374(4)		
Zr(1)-Cent(1)	2.222	Cent(1)-Zr(1)-Cent(2)	122.1
Zr(1)-Cent(2)	2.241	Cent(1)-Zr(1)-Cl(1)	107.5
		Cent(2)-Zr(1)-Cl(2)	107.7

Table S.4. Bond lengths [Å] and angles [°] for **(*S*)-2** (CCDC 635262).

Cent(1)-Zr(1)	2.222	C(4)-Zr(1)-Cl(2)	103.22(4)
Cent(2)-Zr(1)	2.241	C(8)-Zr(1)-Cl(1)	103.54(4)
Zr(1)-C(8)	2.4105(15)	C(9)-Zr(1)-Cl(1)	135.86(4)
Zr(1)-C(9)	2.4262(15)	C(4)-Zr(1)-Cl(1)	135.68(4)
Zr(1)-C(4)	2.4301(14)	Cent(1)-Zr(1)-Cent(2)	122.1
Zr(1)-Cl(2)	2.4356(4)	Cent(1)-Zr(1)-Cl(1)	107.5
Zr(1)-Cl(1)	2.4374(4)	Cent(2)-Zr(1)-Cl(2)	107.7
Zr(1)-C(3)	2.4415(14)	Cl(2)-Zr(1)-Cl(1)	104.467(15)
Zr(1)-C(5)	2.5536(16)	C(8)-Zr(1)-C(3)	68.28(5)
Zr(1)-C(2)	2.5676(15)	C(9)-Zr(1)-C(3)	78.61(5)
Zr(1)-C(7)	2.6051(16)	C(4)-Zr(1)-C(3)	34.84(5)
Zr(1)-C(10)	2.6285(15)	Cl(2)-Zr(1)-C(3)	135.18(4)
Zr(1)-C(1)	2.6629(16)	Cl(1)-Zr(1)-C(3)	104.45(4)
Zr(1)-C(6)	2.6757(16)	C(8)-Zr(1)-C(5)	112.69(5)
Si(1)-C(24)	1.8603(17)	C(9)-Zr(1)-C(5)	96.20(5)
Si(1)-C(25)	1.8702(18)	C(4)-Zr(1)-C(5)	33.02(6)
Si(1)-C(3)	1.8774(16)	Cl(2)-Zr(1)-C(5)	80.54(4)
Si(1)-C(8)	1.8875(17)	Cl(1)-Zr(1)-C(5)	122.09(4)
Si(2)-C(27)	1.8603(18)	C(3)-Zr(1)-C(5)	55.10(5)
Si(2)-C(26)	1.8673(18)	C(8)-Zr(1)-C(2)	96.03(6)
Si(2)-C(4)	1.8762(16)	C(9)-Zr(1)-C(2)	111.72(5)
Si(2)-C(9)	1.8930(17)	C(4)-Zr(1)-C(2)	55.06(5)
C(1)-C(5)	1.414(2)	Cl(2)-Zr(1)-C(2)	123.14(4)
C(1)-C(2)	1.420(2)	Cl(1)-Zr(1)-C(2)	80.80(3)
C(1)-C(11)	1.519(2)	C(3)-Zr(1)-C(2)	33.11(5)
C(2)-C(3)	1.433(2)	C(5)-Zr(1)-C(2)	52.66(5)
C(3)-C(4)	1.459(2)	C(8)-Zr(1)-C(7)	32.79(5)
C(4)-C(5)	1.421(2)	C(9)-Zr(1)-C(7)	55.21(5)
C(6)-C(7)	1.416(2)	C(4)-Zr(1)-C(7)	112.44(6)
C(6)-C(10)	1.419(2)	Cl(2)-Zr(1)-C(7)	121.19(4)
C(7)-C(8)	1.428(2)	Cl(1)-Zr(1)-C(7)	80.92(4)
C(7)-C(18)	1.517(2)	C(3)-Zr(1)-C(7)	96.65(5)
C(8)-C(9)	1.480(2)	C(5)-Zr(1)-C(7)	145.46(5)
C(9)-C(10)	1.432(2)	C(2)-Zr(1)-C(7)	115.58(6)
C(10)-C(21)	1.515(2)	C(8)-Zr(1)-C(10)	55.07(5)
C(11)-C(12)	1.544(2)	C(9)-Zr(1)-C(10)	32.61(5)
C(11)-C(14)	1.571(2)	C(4)-Zr(1)-C(10)	95.71(5)
C(12)-C(13)	1.531(2)	Cl(2)-Zr(1)-C(10)	79.76(4)
C(14)-C(16)	1.528(2)	Cl(1)-Zr(1)-C(10)	122.77(3)
C(14)-C(17)	1.534(2)	C(3)-Zr(1)-C(10)	111.21(5)
C(14)-C(15)	1.535(2)	C(5)-Zr(1)-C(10)	114.95(5)
C(18)-C(19)	1.521(2)	C(2)-Zr(1)-C(10)	144.33(5)
C(18)-C(20)	1.532(3)	C(7)-Zr(1)-C(10)	52.35(5)
C(21)-C(23)	1.531(2)	C(8)-Zr(1)-C(1)	122.54(6)
C(21)-C(22)	1.539(2)	C(9)-Zr(1)-C(1)	122.24(5)
		C(4)-Zr(1)-C(1)	54.14(5)
C(8)-Zr(1)-C(9)	35.63(5)	Cl(2)-Zr(1)-C(1)	91.84(4)
C(8)-Zr(1)-C(4)	79.68(6)	Cl(1)-Zr(1)-C(1)	91.01(4)
C(9)-Zr(1)-C(4)	68.11(5)	C(3)-Zr(1)-C(1)	54.27(5)
C(8)-Zr(1)-Cl(2)	134.63(4)	C(5)-Zr(1)-C(1)	31.35(5)
C(9)-Zr(1)-Cl(2)	102.63(4)	C(2)-Zr(1)-C(1)	31.44(5)

C(7)-Zr(1)-C(1)	146.97(5)	Si(2)-C(4)-Zr(1)	95.74(6)
C(10)-Zr(1)-C(1)	146.21(5)	C(1)-C(5)-C(4)	110.36(15)
C(8)-Zr(1)-C(6)	53.71(5)	C(1)-C(5)-Zr(1)	78.59(10)
C(9)-Zr(1)-C(6)	53.65(5)	C(4)-C(5)-Zr(1)	68.71(8)
C(4)-Zr(1)-C(6)	121.76(5)	C(7)-C(6)-C(10)	109.05(14)
Cl(2)-Zr(1)-C(6)	90.36(4)	C(7)-C(6)-Zr(1)	71.71(9)
Cl(1)-Zr(1)-C(6)	91.97(4)	C(10)-C(6)-Zr(1)	72.65(9)
C(3)-Zr(1)-C(6)	121.93(5)	C(6)-C(7)-C(8)	108.61(14)
C(5)-Zr(1)-C(6)	145.92(5)	C(6)-C(7)-C(18)	123.55(14)
C(2)-Zr(1)-C(6)	146.50(6)	C(8)-C(7)-C(18)	127.58(15)
C(7)-Zr(1)-C(6)	31.07(5)	C(6)-C(7)-Zr(1)	77.22(9)
C(10)-Zr(1)-C(6)	31.02(5)	C(8)-C(7)-Zr(1)	66.09(8)
C(1)-Zr(1)-C(6)	175.74(5)	C(18)-C(7)-Zr(1)	127.32(11)
C(24)-Si(1)-C(25)	107.60(9)	C(7)-C(8)-C(9)	106.95(14)
C(24)-Si(1)-C(3)	108.97(8)	C(7)-C(8)-Si(1)	128.51(11)
C(25)-Si(1)-C(3)	117.50(8)	C(9)-C(8)-Si(1)	121.15(12)
C(24)-Si(1)-C(8)	115.62(7)	C(7)-C(8)-Zr(1)	81.12(9)
C(25)-Si(1)-C(8)	114.16(8)	C(9)-C(8)-Zr(1)	72.76(9)
C(3)-Si(1)-C(8)	92.65(7)	Si(1)-C(8)-Zr(1)	95.63(6)
C(24)-Si(1)-Zr(1)	105.40(6)	C(10)-C(9)-C(8)	106.75(13)
C(25)-Si(1)-Zr(1)	147.00(6)	C(10)-C(9)-Si(2)	126.49(12)
C(3)-Si(1)-Zr(1)	49.40(4)	C(8)-C(9)-Si(2)	122.93(12)
C(8)-Si(1)-Zr(1)	48.48(5)	C(10)-C(9)-Zr(1)	81.49(9)
C(27)-Si(2)-C(26)	107.37(8)	C(8)-C(9)-Zr(1)	71.60(8)
C(27)-Si(2)-C(4)	116.02(8)	Si(2)-C(9)-Zr(1)	95.42(7)
C(26)-Si(2)-C(4)	109.16(8)	C(6)-C(10)-C(9)	108.45(14)
C(27)-Si(2)-C(9)	116.31(8)	C(6)-C(10)-C(21)	124.29(13)
C(26)-Si(2)-C(9)	115.14(8)	C(9)-C(10)-C(21)	126.90(13)
C(4)-Si(2)-C(9)	92.35(7)	C(6)-C(10)-Zr(1)	76.33(9)
C(27)-Si(2)-Zr(1)	147.28(6)	C(9)-C(10)-Zr(1)	65.91(8)
C(26)-Si(2)-Zr(1)	105.26(6)	C(21)-C(10)-Zr(1)	128.92(11)
C(4)-Si(2)-Zr(1)	48.77(4)	C(1)-C(11)-C(12)	113.31(13)
C(9)-Si(2)-Zr(1)	48.70(5)	C(1)-C(11)-C(14)	110.41(13)
C(5)-C(1)-C(2)	106.57(15)	C(12)-C(11)-C(14)	113.72(14)
C(5)-C(1)-C(11)	127.81(16)	C(13)-C(12)-C(11)	112.31(14)
C(2)-C(1)-C(11)	125.15(14)	C(16)-C(14)-C(17)	108.46(13)
C(5)-C(1)-Zr(1)	70.05(9)	C(16)-C(14)-C(15)	108.26(14)
C(2)-C(1)-Zr(1)	70.57(9)	C(17)-C(14)-C(15)	108.93(14)
C(11)-C(1)-Zr(1)	130.28(11)	C(16)-C(14)-C(11)	110.67(15)
C(1)-C(2)-C(3)	109.96(13)	C(17)-C(14)-C(11)	111.85(13)
C(1)-C(2)-Zr(1)	77.99(9)	C(15)-C(14)-C(11)	108.59(13)
C(3)-C(2)-Zr(1)	68.61(8)	C(7)-C(18)-C(19)	112.72(15)
C(2)-C(3)-C(4)	106.28(14)	C(7)-C(18)-C(20)	108.41(15)
C(2)-C(3)-Si(1)	125.09(12)	C(19)-C(18)-C(20)	110.16(15)
C(4)-C(3)-Si(1)	123.41(12)	C(10)-C(21)-C(23)	111.75(13)
C(2)-C(3)-Zr(1)	78.28(9)	C(10)-C(21)-C(22)	108.05(14)
C(4)-C(3)-Zr(1)	72.15(8)	C(23)-C(21)-C(22)	110.17(14)
Si(1)-C(3)-Zr(1)	94.88(6)		
C(5)-C(4)-C(3)	106.83(13)		
C(5)-C(4)-Si(2)	126.78(12)		
C(3)-C(4)-Si(2)	121.96(12)		
C(5)-C(4)-Zr(1)	78.27(9)		
C(3)-C(4)-Zr(1)	73.01(8)		

Table S.5. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for **(*S*)-2** (CCDC 635262).

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	88(1)	102(1)	75(1)	0(1)	-3(1)	7(1)
Cl(1)	171(2)	199(2)	97(1)	5(1)	-23(1)	10(2)
Cl(2)	134(2)	129(2)	148(2)	-8(1)	25(1)	24(1)
Si(1)	109(2)	108(2)	116(2)	1(2)	4(2)	9(1)
Si(2)	102(2)	127(2)	83(2)	12(2)	-11(1)	-9(2)
C(1)	93(6)	108(8)	110(6)	0(5)	1(5)	-3(5)
C(2)	82(6)	140(8)	121(6)	4(6)	12(5)	8(6)
C(3)	74(5)	127(8)	122(6)	-5(6)	1(5)	1(5)
C(4)	72(6)	137(8)	102(6)	-1(6)	-19(4)	-11(6)
C(5)	91(6)	132(8)	103(6)	-6(6)	-12(5)	-4(5)
C(6)	108(6)	156(9)	119(6)	-7(6)	-4(5)	-8(5)
C(7)	138(6)	111(8)	135(6)	15(7)	1(6)	-25(5)
C(8)	143(6)	86(7)	72(5)	8(5)	7(6)	-7(6)
C(9)	132(7)	97(8)	99(6)	11(5)	-1(5)	-14(5)
C(10)	112(6)	109(8)	98(6)	7(6)	2(5)	-11(6)
C(11)	142(7)	106(8)	85(6)	16(5)	3(5)	4(6)
C(12)	173(8)	126(9)	133(7)	12(6)	10(6)	21(6)
C(13)	208(9)	192(10)	218(8)	14(7)	-41(6)	86(7)
C(14)	147(7)	130(8)	99(6)	22(5)	8(5)	-6(5)
C(15)	231(9)	187(9)	165(7)	47(6)	39(7)	-25(7)
C(16)	141(7)	191(10)	178(8)	14(6)	21(6)	7(6)
C(17)	171(7)	162(8)	181(6)	-2(7)	-16(8)	-37(7)
C(18)	135(7)	170(9)	134(7)	-59(6)	1(5)	-27(6)
C(19)	143(8)	294(11)	162(8)	-74(7)	-41(6)	-14(7)
C(20)	276(10)	163(10)	274(10)	-68(8)	-42(8)	-58(8)
C(21)	112(6)	140(8)	105(6)	-12(5)	18(5)	2(5)
C(22)	204(8)	178(10)	140(7)	26(6)	42(6)	28(7)
C(23)	125(7)	184(9)	166(7)	-16(7)	19(5)	14(6)
C(24)	154(7)	186(10)	147(7)	-49(6)	10(6)	-3(7)
C(25)	241(9)	160(10)	190(8)	17(7)	-2(7)	60(7)
C(26)	155(8)	205(10)	154(7)	-32(6)	-12(6)	-23(7)
C(27)	159(8)	202(10)	131(7)	44(6)	-38(6)	-12(7)

Results from unidirectional site epimerization model

Below is a graphical summary of the fits from the unidirectional site epimerization model used to model polypropylene pentad data. For a complete derivation of the model and a more extensive discussion see S. A. Miller's Ph. D. Thesis (California Institute of Technology, 2000). The model considers three parameters that can affect the polymer pentads: enantiofacial selectivity of olefin insertion from the two sites of the catalyst (α and β) and the probability of site epimerization during polymerization (ε). The statistical model calculates the probability of every stereochemical outcome (manifested in the polypropylene pentads) at a given α, β, and ε. Theoretical fits to the experimental data were obtained using Excel by iteratively changing α, β, and ε until the root mean square (RMS) difference between the experimental and theoretical pentads was minimized.

Below is a bar chart for each polypropylene sample in Table 2 that shows the theoretical and experimental pentads along with the RMS value for: a) a model where all three parameters are varied and b) a model where only ε is varied using α and β obtained from neat polypropylene data (Note: xmrx = rmrr + mmrm).

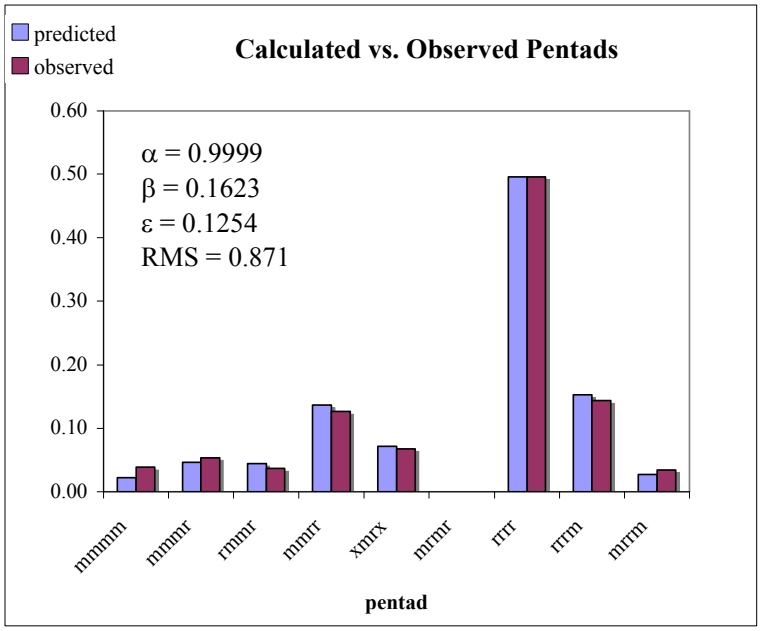


Figure S.2 Unimolecular site epimerization model fits for polypropylene (neat C_3H_6) with catalyst **(*S*)-1** (Table 2, entry 9) varying all three parameters.

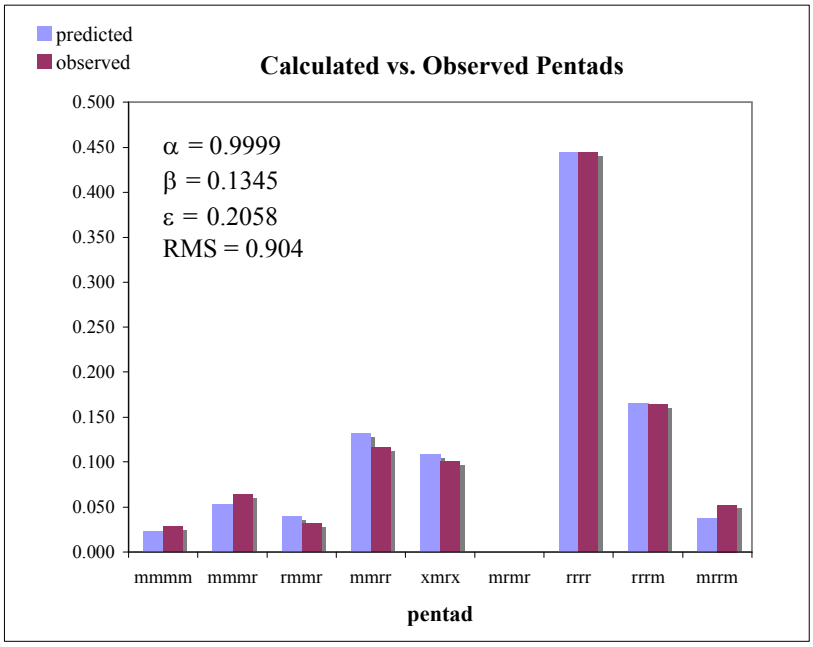
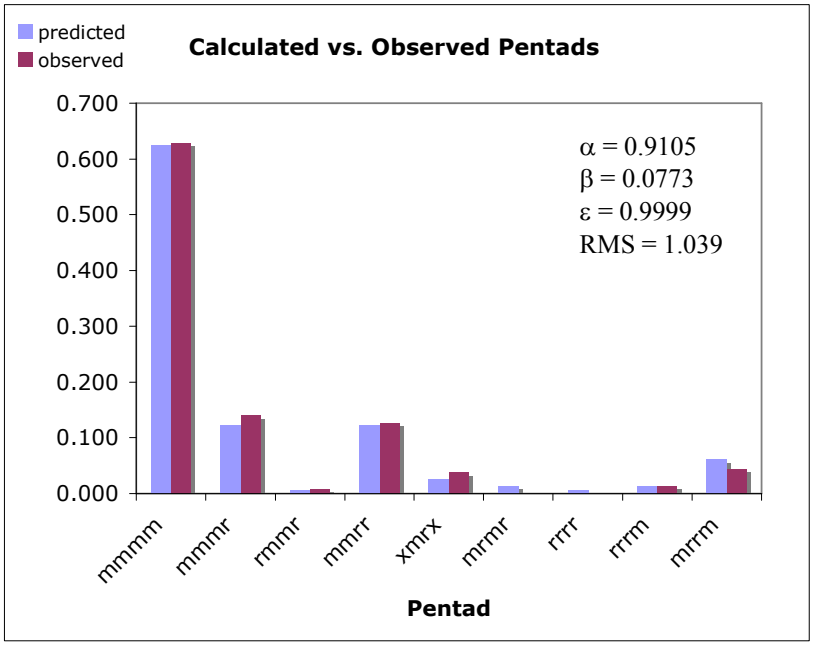


Figure S.3 Unimolecular site epimerization model fits for polypropylene (neat C_3H_6) with catalyst **(*S*)-2** (Table 2, entry 10) varying all three parameters.

(a) 3-parameter, 0.8 M C_3H_6, ***(S)*-1**



(b) 1-parameter, 0.8 M C_3H_6, ***(S)*-1**

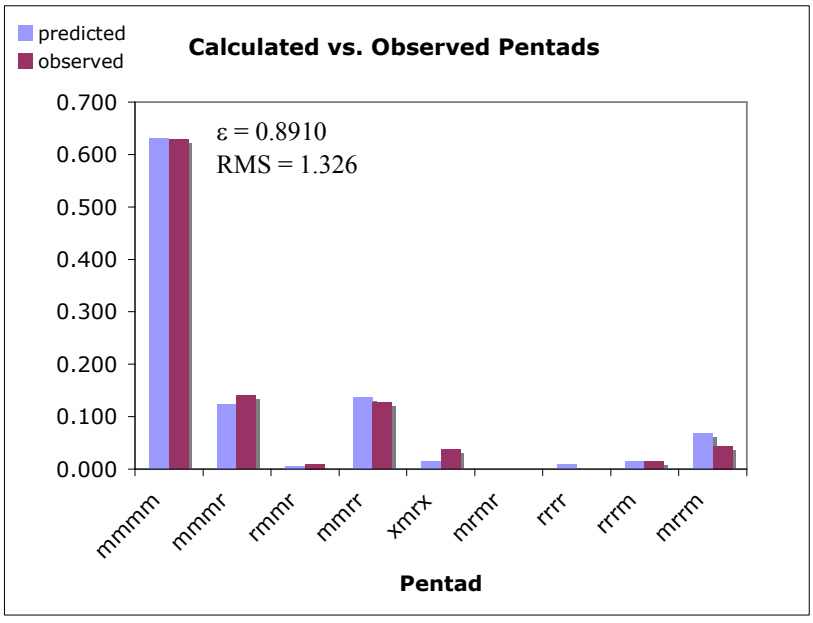
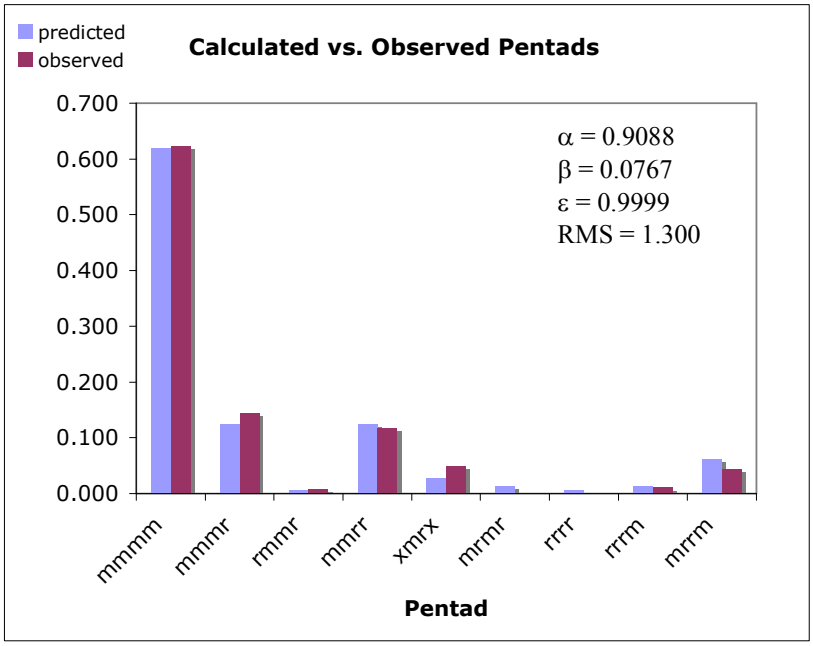


Figure S.4 Unimolecular site epimerization model fits for polypropylene with catalyst ***(S)*-1** (Table 2, entry 1) varying (a) all three parameters and (b) only ε using α = 0.9999 and β = 0.1623 from Figure S.1.

a) 3-paramter, 0.8 M C_3H_6, **(*S*)-2**



b) 1-parameter, 0.8 M, **(*S*)-2**

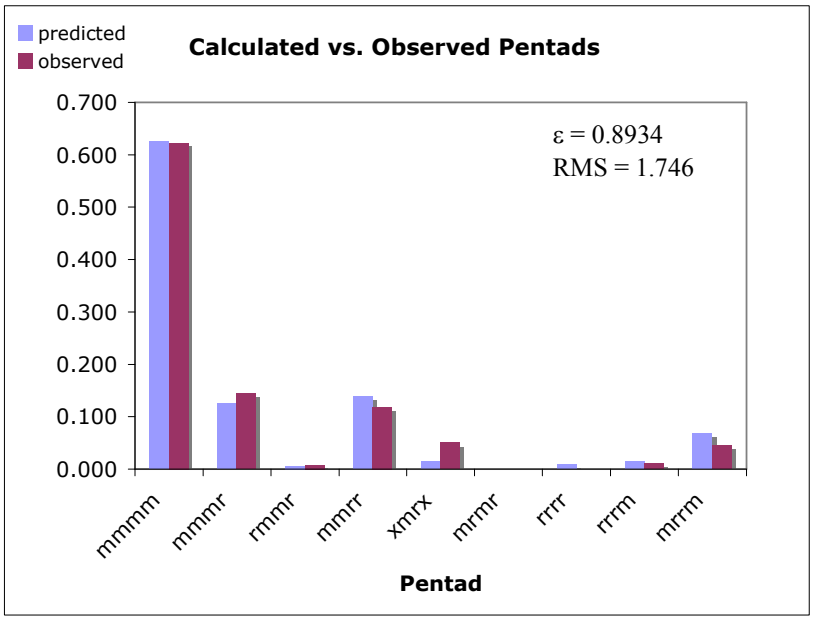
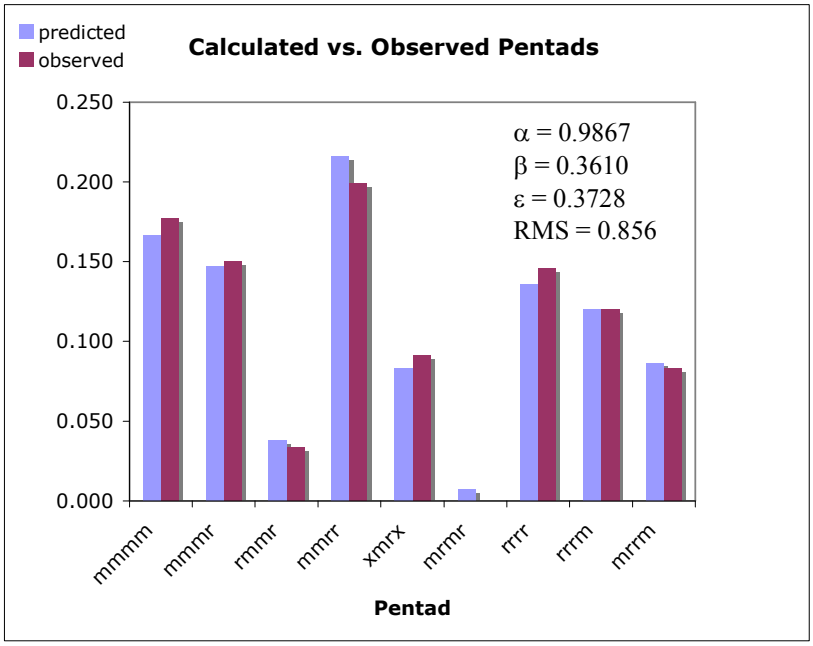


Figure S.5 Unimolecular site epimerization model fits for polypropylene (0.8 M) with catalyst **(*S*)-2** (Table 2, entry 2) varying (a) all three parameters and (b) only ε using α = 0.9999 and β = 0.1345 from Figure S.2.

(a) 3-parameter, 3.4 M C_3H_6, **(*S*)-1**



(b) 1-parameter, 3.4 M C_3H_6, **(*S*)-1**

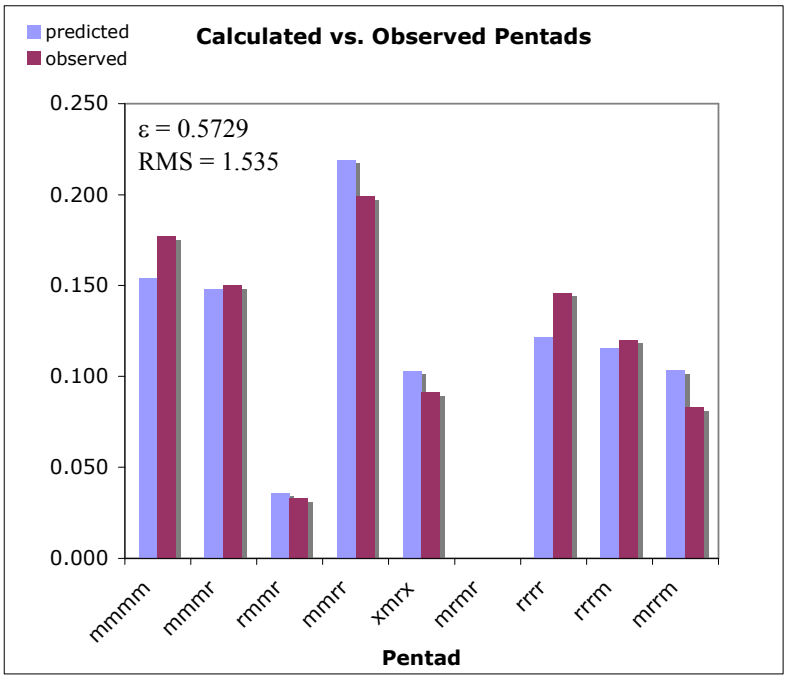
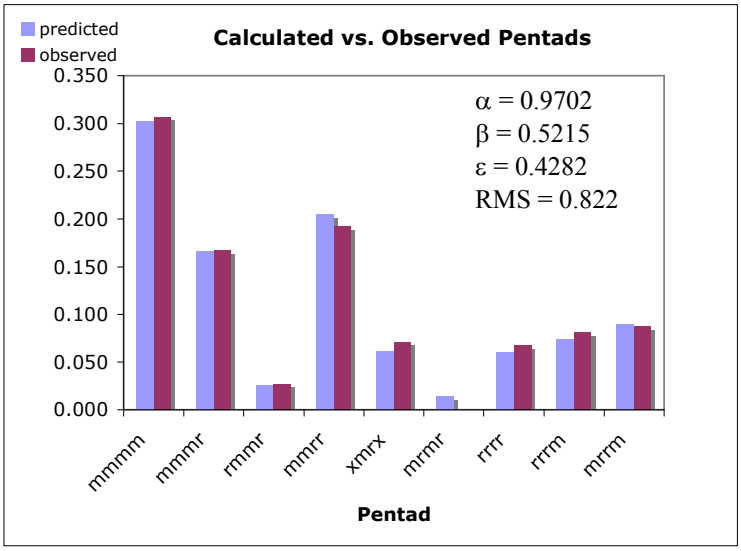


Figure S.6 Unimolecular site epimerization model fits for polypropylene (3.4 M) with catalyst **(*S*)-1** (Table 2, entry 3) varying (a) all three parameters and (b) only ε using α = 0.9999 and β = 0.1623 from Figure S.1..

a) 3-parameter, 3.4 M C_3H_6, **(*S*)-2**



b) 1-paramter, 3.4 M C_3H_6, **(*S*)-2**

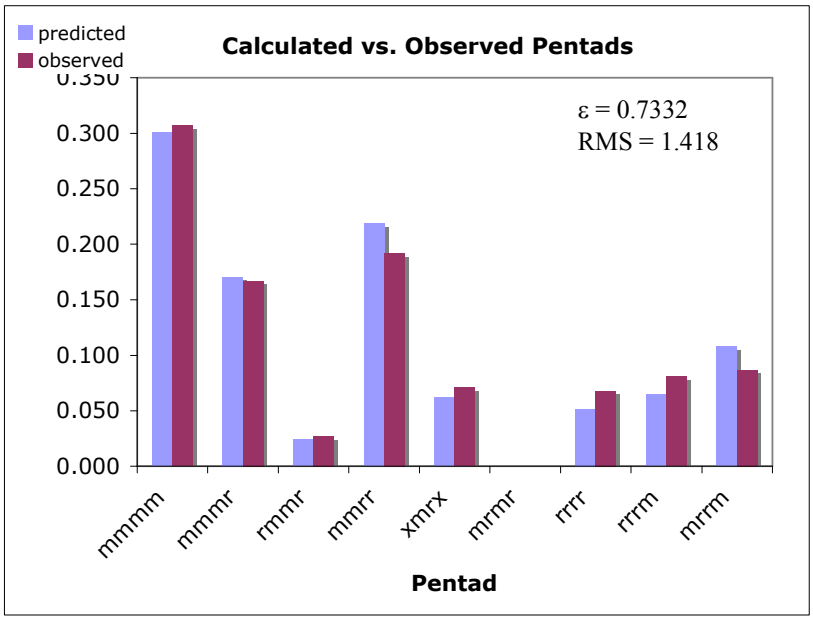
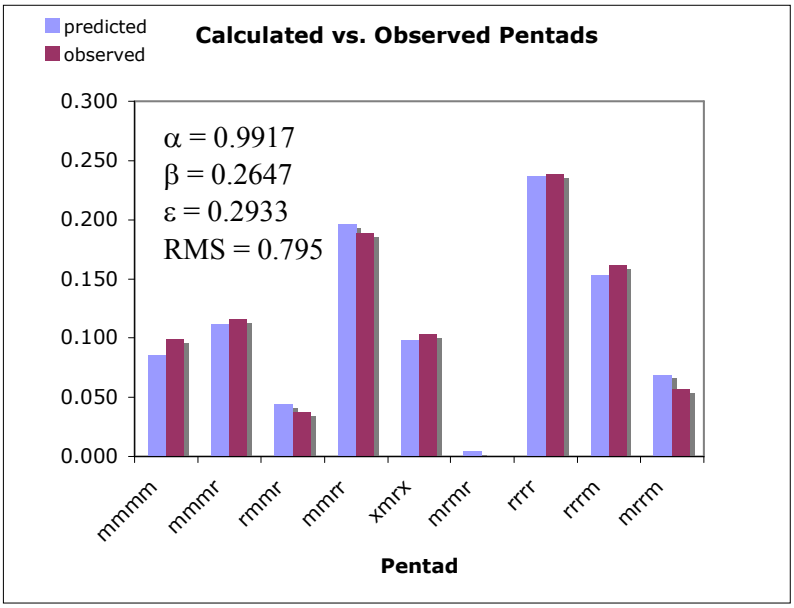


Figure S.7 Unimolecular site epimerization model fits for polypropylene (3.4 M) with catalyst **(*S*)-2** (Table 2, entry 4) varying (a) all three parameters and (b) only ε using α = 0.9999 and β = 0.1345 from Figure S.2.

(a) 3-parameter, 4.6 M C_3H_6, **(*S*)-1**



(b) 1-parameter, 4.6 C_3H_6, **(*S*)-1**

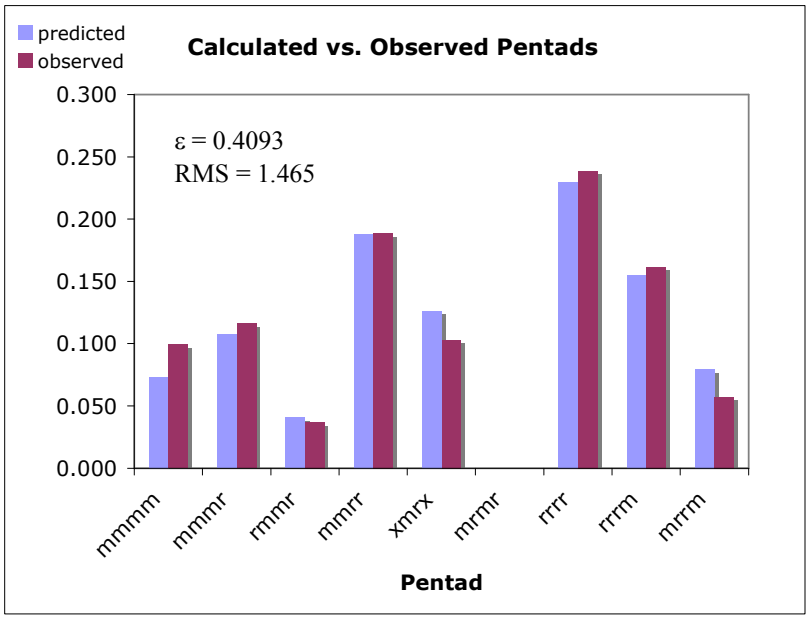
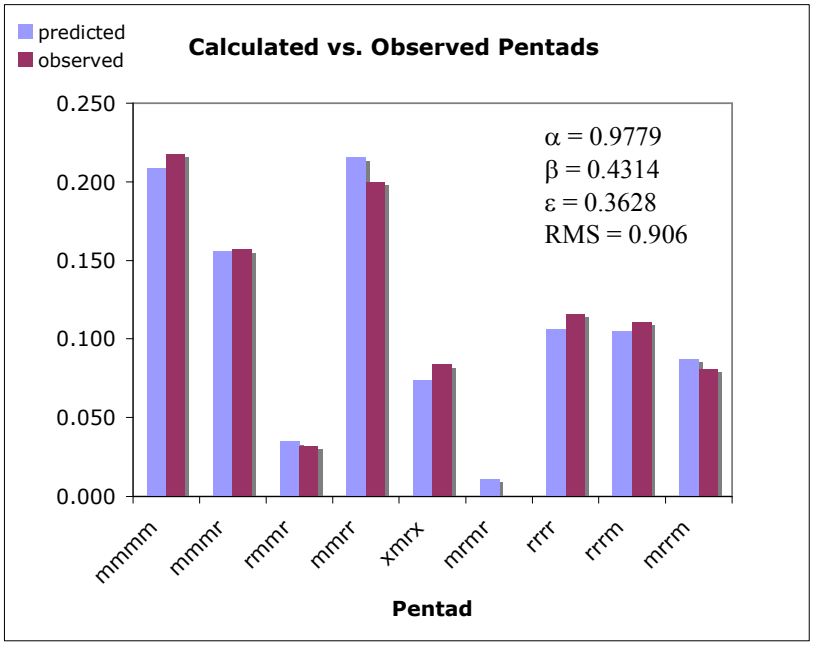


Figure S.8 Unimolecular site epimerization model fits for polypropylene (4.6 M) with catalyst **(*S*)-1** (Table 1, entry 5) varying (a) all three parameters and (b) only ε using α = 0.9999 and β = 0.1623 from Figure S.1.

a) 3-parameter, 4.6 M C_3H_6, **(*S*)-2**



b) 1-parameter, 4.6 M C_3H_6, **(*S*)-2**

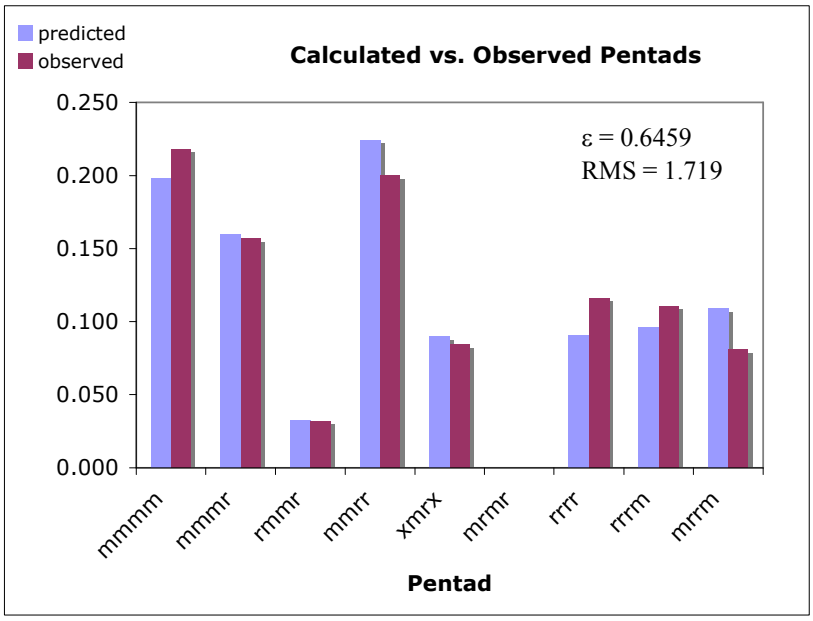
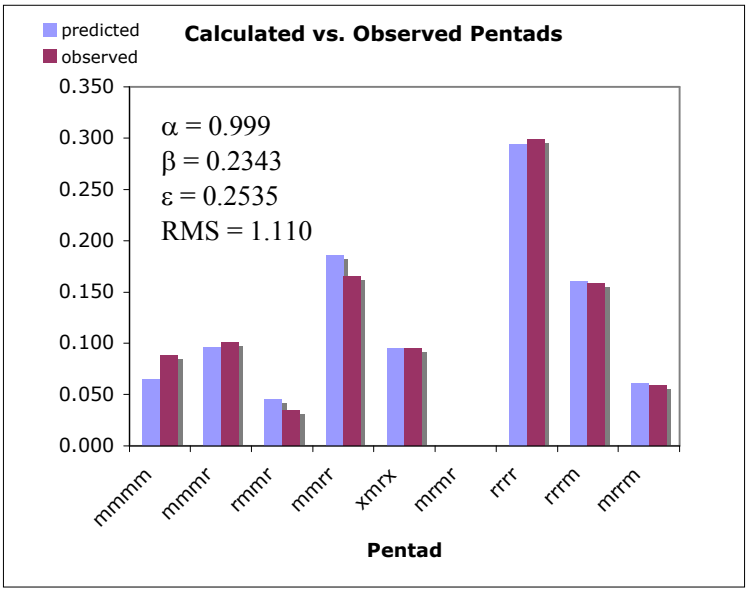


Figure S.9 Unimolecular site epimerization model fits for polypropylene (4.6 M) with catalyst **(*S*)-2** (Table 2, entry 6) varying (a) all three parameters and (b) only ε using α = 0.9999 and β = 0.1345 from Figure S.2.

(a) 3-parameter, 8.1 M C_3H_6, **(*S*)-1**



(b) 1-paramater, 8.1 C_3H_6, **(*S*)-1**

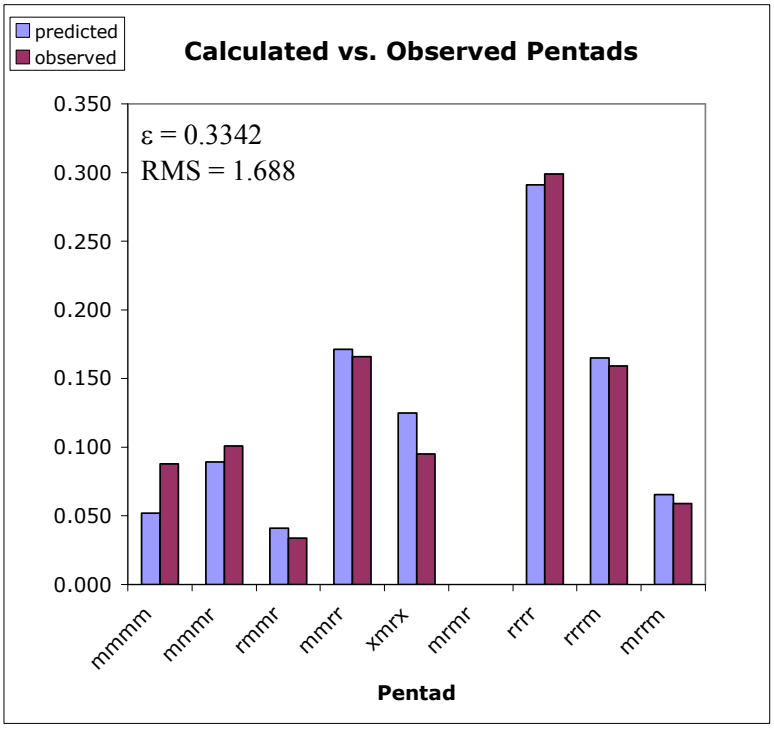
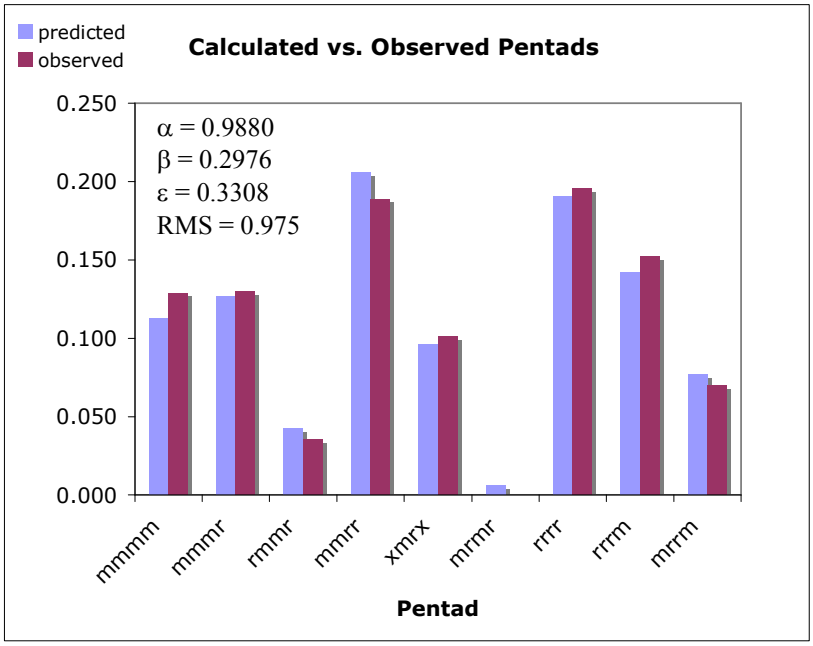


Figure S.10 Unimolecular site epimerization model fits for polypropylene (8.1 M) with catalyst **(*S*)-1** (Table 2, entry 7) varying (a) all three parameters and (b) only ε using α = 0.9999 and β = 0.1623 from Figure S.1.

(a) 3-paramater, 8.1 M C_3H_6, **(*S*)-2**



(b) 1-parameter, 8.1 M C_3H_6, **(*S*)-2**

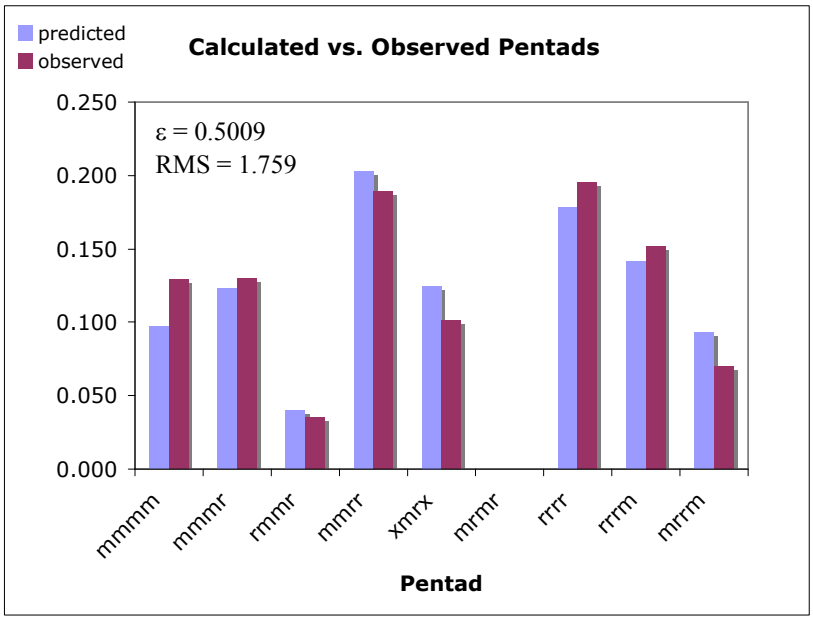


Figure S.11 Unimolecular site epimerization model fits for polypropylene (8.1 M) with catalyst **(*S*)-2** (Table 2, entry 8) varying (a) all three parameters and (b) only ε using α = 0.9999 and β = 0.1345 from Figure S.2.